

Developing Methodology to Prepare a Nanoparticle Coated Crystal for Infrared Analyses

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Abstract

The purpose of my research is to develop a method to prepare a nanoparticle coated crystal for infrared (IR) analyses in order to specifically identify changes to molecules that coat the surface. The two nanomaterials analyzed in this study were hematite ($\alpha\text{-Fe}_2\text{O}_3$) and nanosilver. Citrate was the primary coating agent used on both materials. The hematite and nanosilver were synthesized and characterized using a transmission electron microscope. The particles were coated to IR crystals and the adsorption of the coating layers was evaluated under static and dynamic conditions. Variables included coating agent (water, citrate, phthalic acid) and pH.

The greatest issue to overcome was the presence of water in the spectra. The methodology developed would conceptually be applicable to a multitude of nanomaterials and coating agents.

Objectives

- Develop a method to prepare a nanoparticle coated IR surface
- Couple this to a flow-through cell for dynamic changes
- Implement the method for analysis and validation

Background

Nanoparticle Risk Assessment

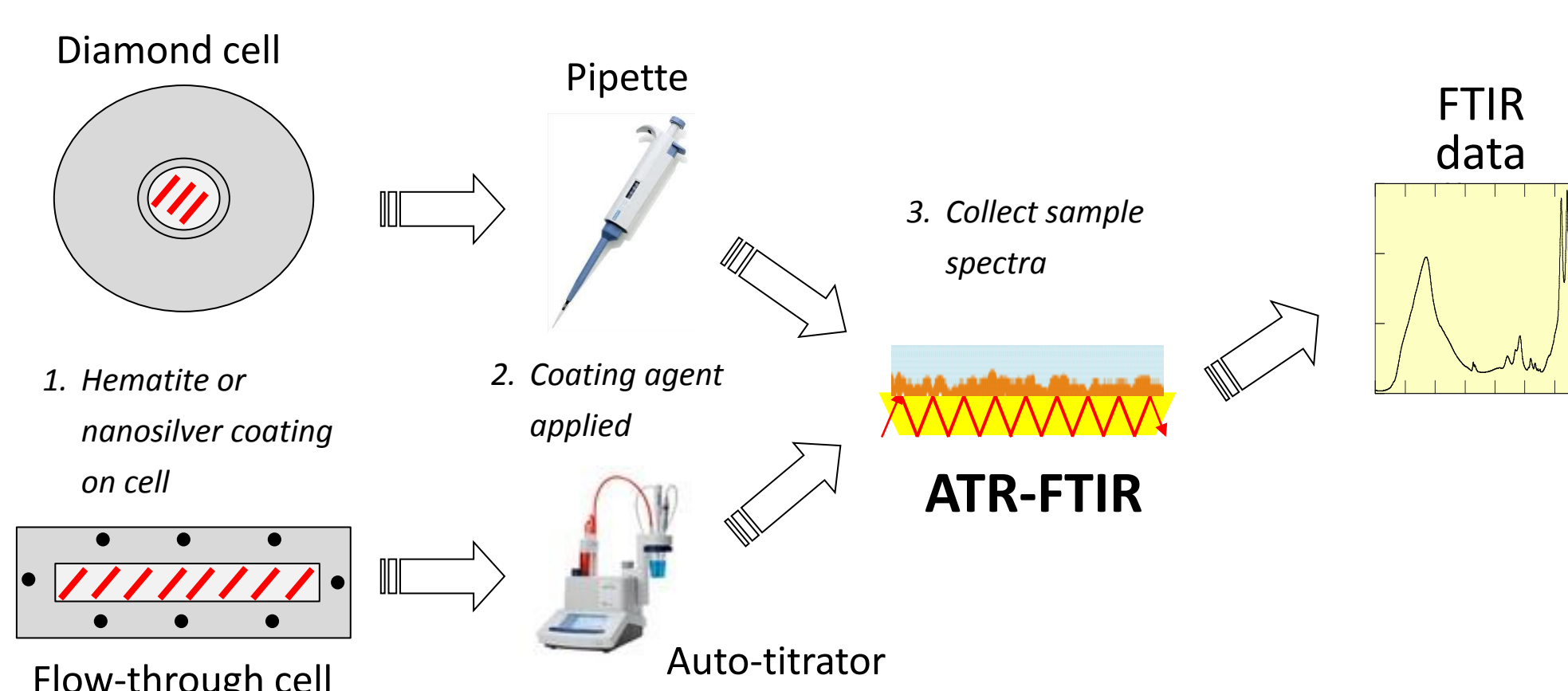
- Nanoscience and nanotechnology involve the synthesis, assembly, manipulation, and application of materials on the nanometer-scale level that spans approximately 1 to 100 nm at two- or three-dimensions [1].
- The high surface area to volume ratio of the nanoparticles results in high reactivity which leads to particle aggregation and settling, negating the desired properties. To prevent particle aggregation, a coating or capping agent is applied either during or post synthesis. As nanomaterials are inevitably introduced to the environment, it is unknown how their compositions and coating agents alter in different settings and over a prolonged period of time.

ATR-FTIR

- Observed interactions between infrared radiation and the molecule of interest, can help elucidate the structure of the molecule. Similarly, the FTIR spectra from a sorbed sample can be compared the spectra of known structures to determine the mode and structure of the surface complex.

Methodology

Procedure



In the static tests, the diamond crystal was coated with the nanomaterial with an aliquot of capping agent placed on top. When coupled to a flow-through cell for dynamic testing, the crystal was coated and then an HPLC pump directed fluid from the autotitrator to the IR spectrometer and back

Figure 1. layout of dynamic, flow-through system

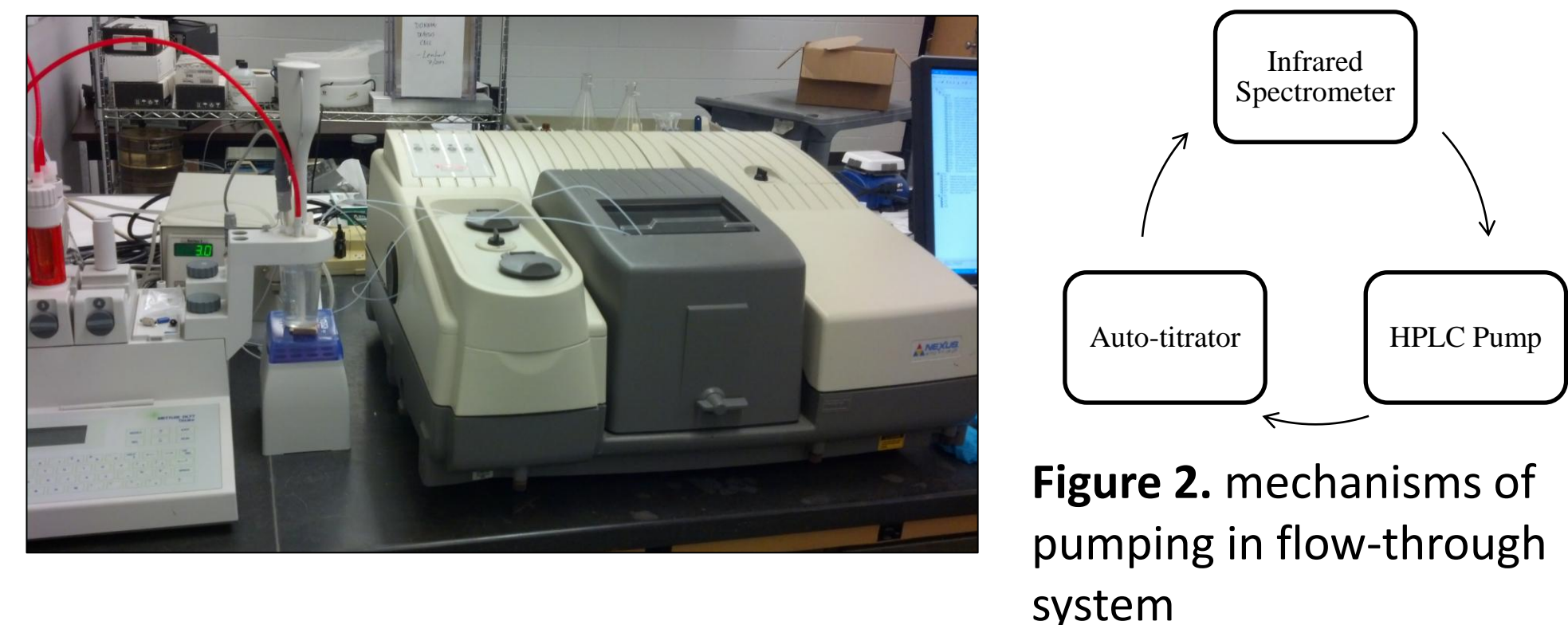


Figure 2. mechanisms of pumping in flow-through system

Materials

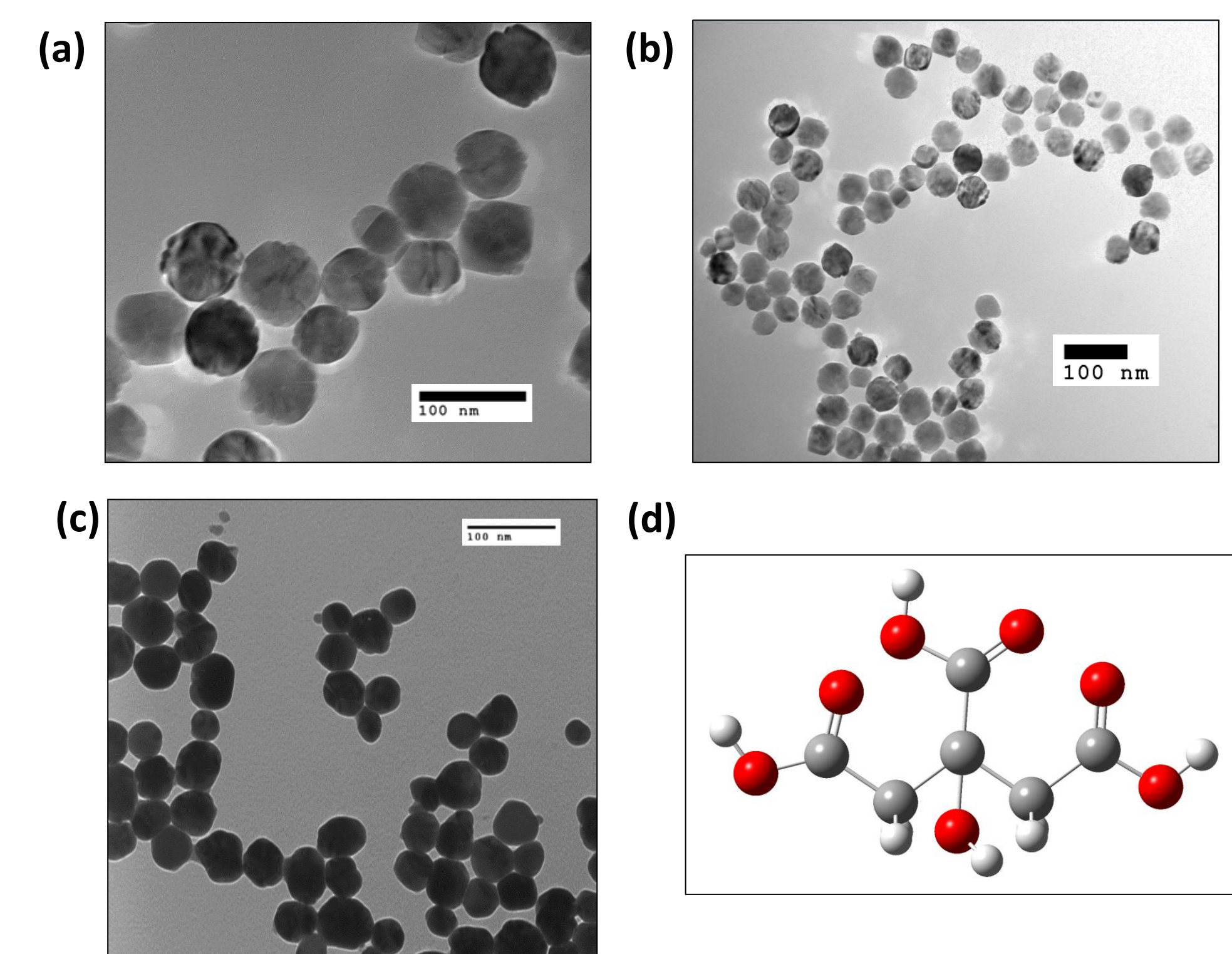


Figure 3. TEM images of synthesized hematite and nanosilver. (a) and (b) hematite with $d=76$ nm (c) nanosilver with $d=46$ nm (d) Citric acid ($pK_{a1} = 3.13$, $pK_{a2} = 4.72$, $pK_{a3} = 6.33$)

Results and Discussion

Previously collected data from batch adsorption experiments of citrate and phthalic acid on hematite were used to test the validity of the static and dynamic systems. The batch adsorption occurred at a much higher concentration and therefore have stronger absorption spectra.

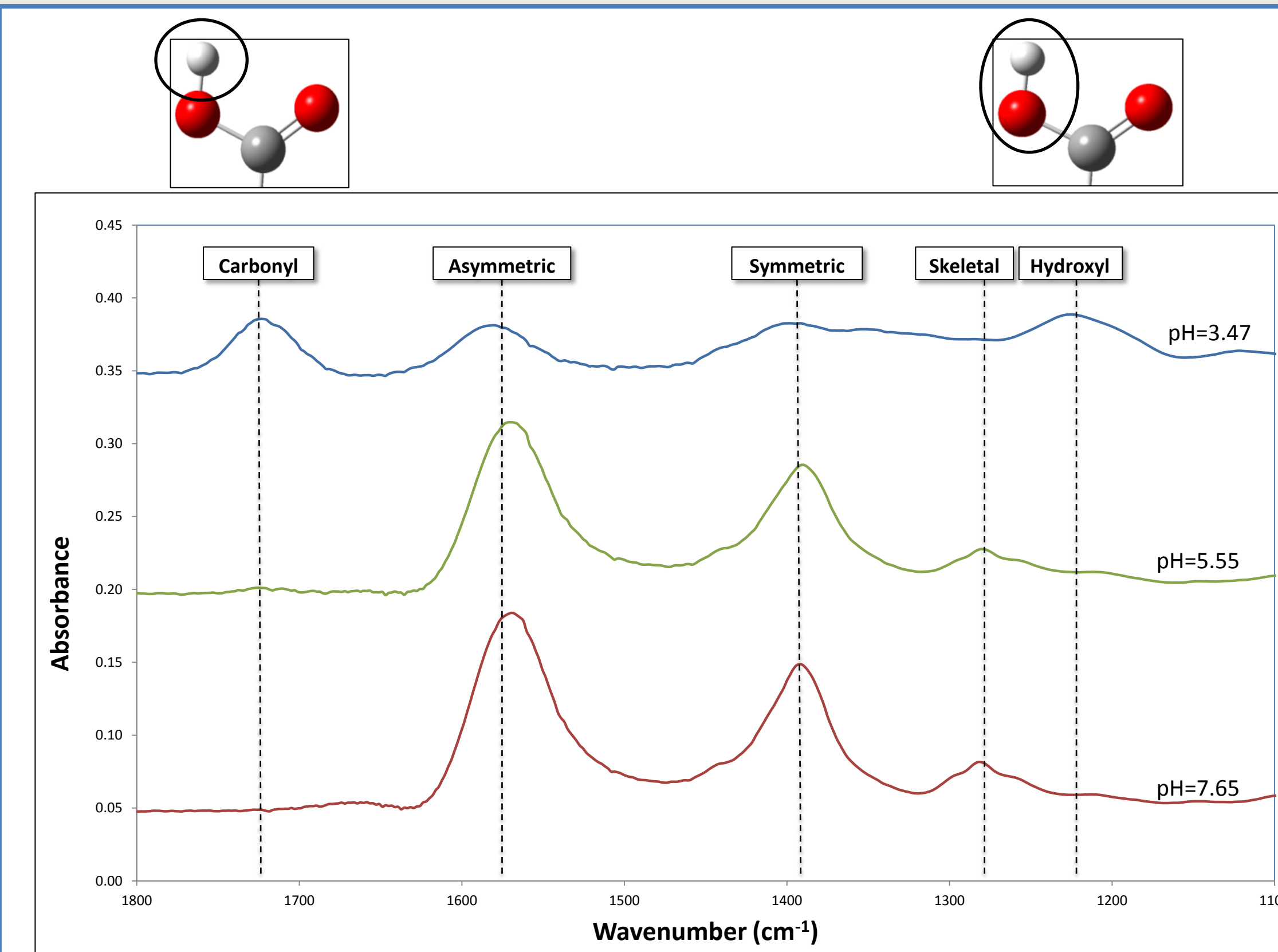


Figure 4. IR spectra of 200mM citrate solution in liquid phase

Static System – Diamond Cell

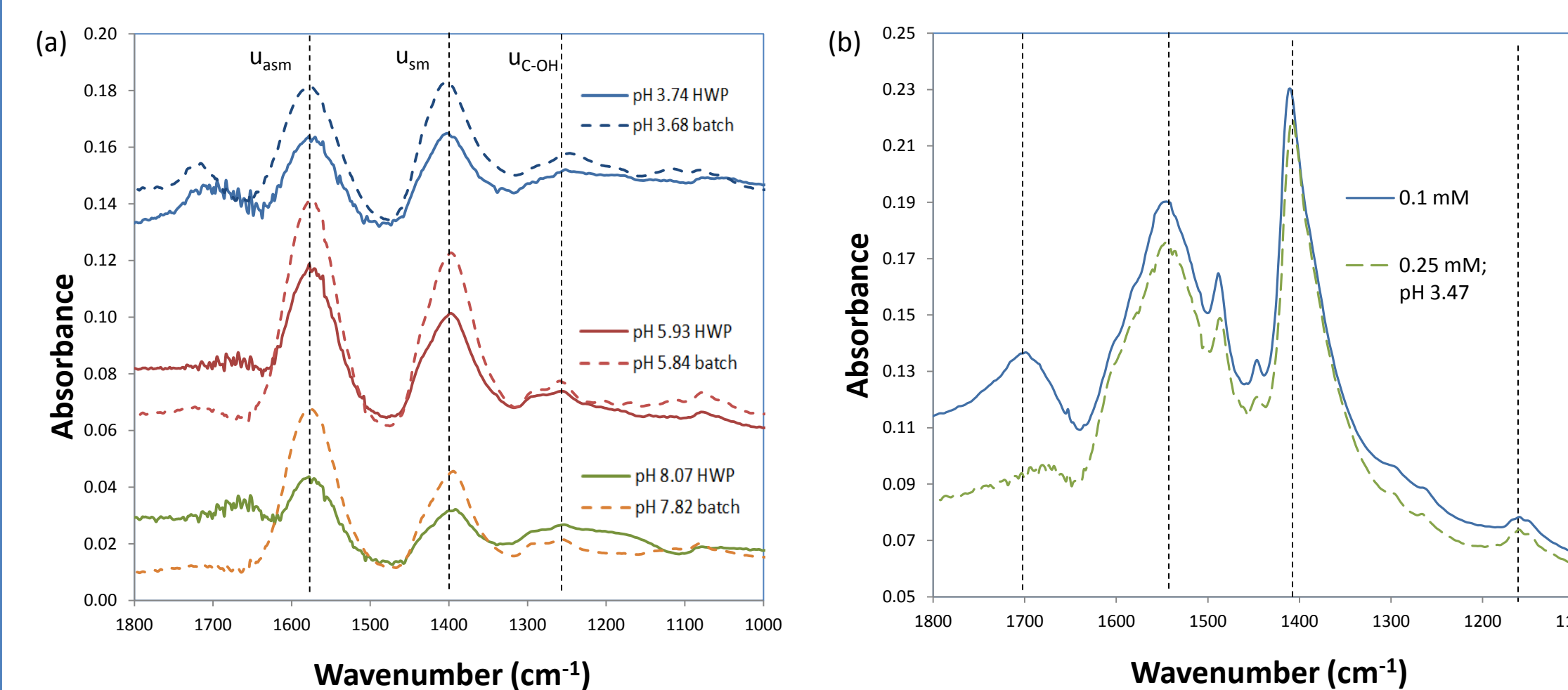


Figure 5. FTIR data from the static experiments: (a) comparison of 1mM citrate on hematite (solid) to previous 1mM citrate batch adsorption experiment (dotted), (b) 0.1mM phthalic acid adsorbed to hematite (solid) vs previous 0.25mM batch adsorption experiment (dotted) and (c) 1mM citrate adsorbed to silver (solid) vs 200mM citrate in solution phase (dotted) as a function of pH. Vertical dotted lines represent relevant peaks observed

- Spectra show that citrate and phthalic acid are successfully detected at the nanoparticle surface.

Dynamic System – Flow through cell

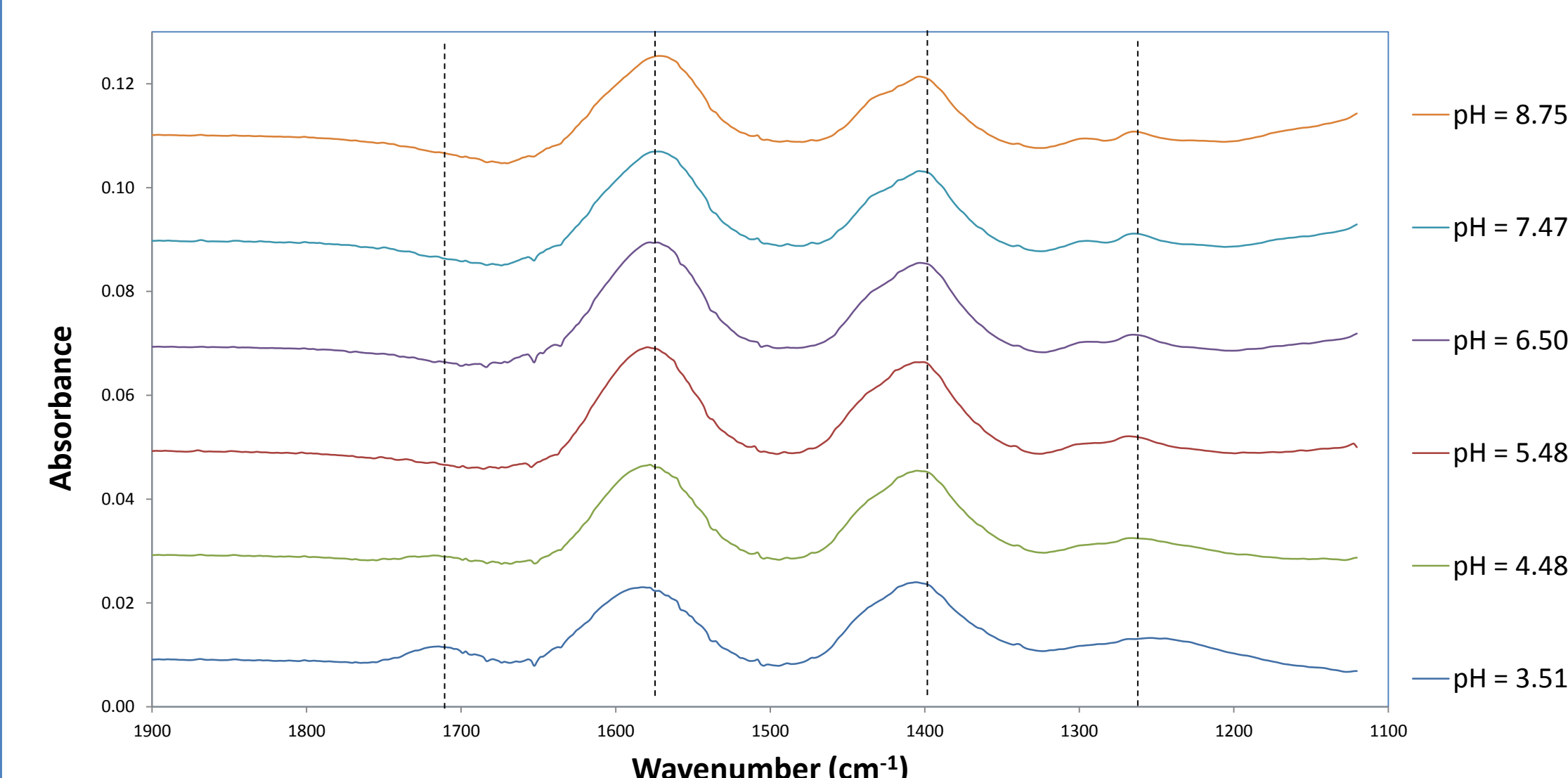


Figure 6. Citrate (1mM + 100mM NaCl) adsorbed to hematite in flow-through cell as a function of pH

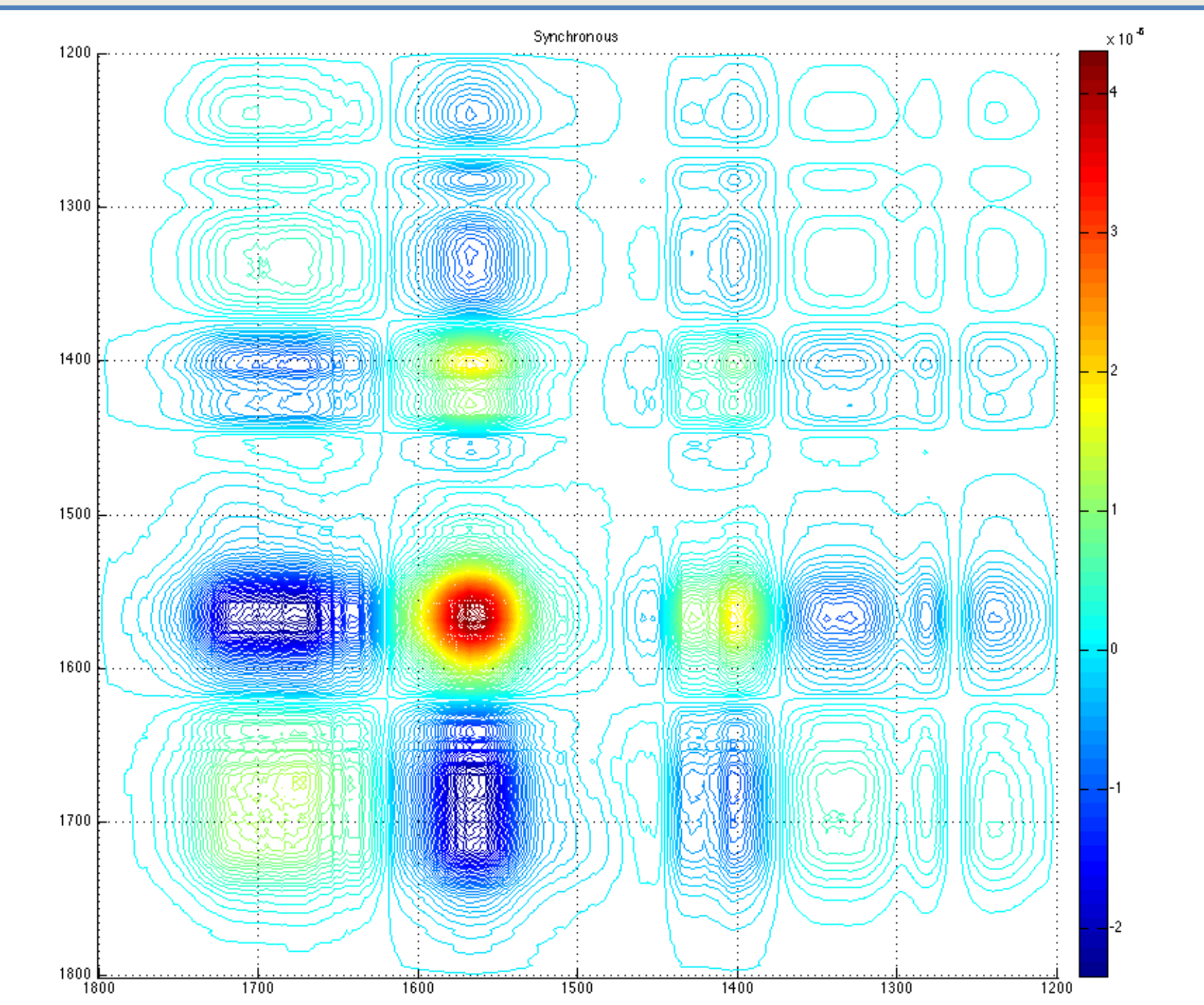


Figure 7. Synchronous 2D correlation plot comparing movement of spectra from 0.1mM citrate solution adsorbed to hematite as pH is increased. Plot shows a strong positive correlation for the asymmetric stretch at 1570 cm^{-1} but an undesired heavy presence of water at 1640 cm^{-1}

- Spectra was not obtained for nanosilver on the flow-through cell. It's possible that the silver does not readily adhere to the germanium crystal surface as it did to the diamond cell in the static system

Summary and Conclusions

- Tracking changes to the molecules that coat the surface of nanomaterials is imperative to understanding the inherent risk when nanomaterials are released to the environment
- The static test was considered a success for both the hematite and silver materials however; accommodations should be made in the future to reduce the influence of water in the spectra
- The optimal method for the flow-through cell was to subtract deionized water spectra from all components before resolving the spectra. A synchronous 2D correlation plot compared the obtained results to a previous batch adsorption experiment and revealed that this method did not completely remove the influence of water and failed to accurately detect the carbonyl group.
- Dynamic tests involving the nanosilver solution were unsuccessful
- The ability to successfully subtract the water absorption of IR will make this method capable of analyzing a multitude of nanomaterials and capping agents. D_2O is not IR active but it is also not cost efficient. Since the flow-through cell does not require much water, substituting D_2O would remove the water peak

References

- [1] Rotello, V.M., Nanoparticles : building blocks for nanotechnology. 2004, New York: Kluwer Academic/Plenum Publishers. p. 284
- [2] Noerpel et al. Unpublished work. 4 Aug. 2011
- [3] Hwang, Yu Sik, Liu, Jin, Lenhart, John J., Hadad, Christopher M., Surface complexes of phthalic acid at the hematite/water interface. Journal of Colloid and Interface Science, 2007. 307(1): p. 124-134.